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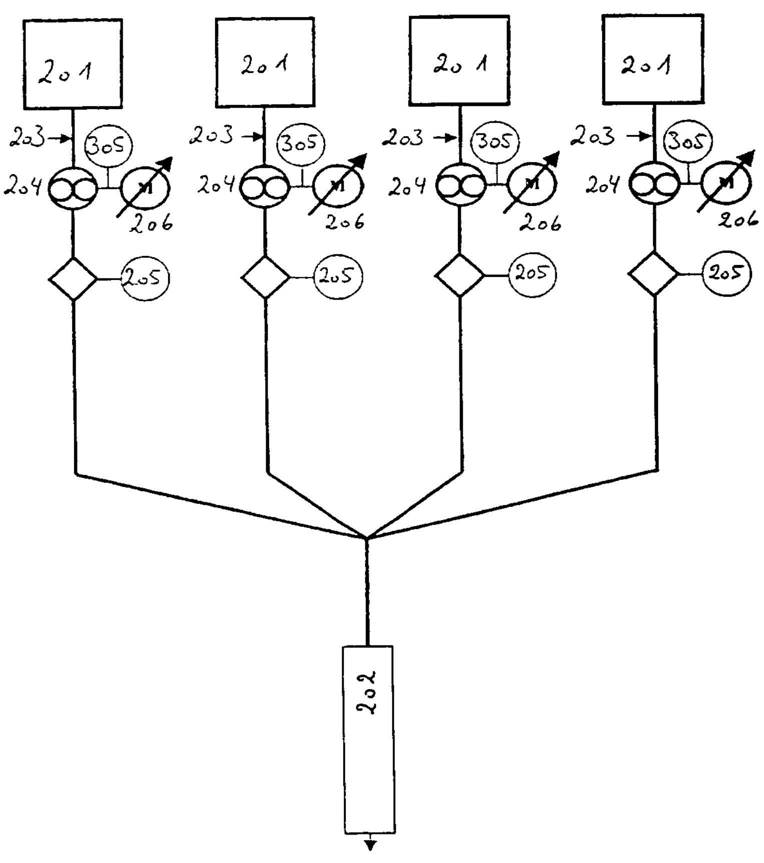
[Continued on next page]

(54) Title: POLYMER PRODUCT WITH CONTINUOUSLY GRADUATED HARDNESS



(57) Abstract: Method for production of a polymer product with varying hardness comprising adding together and mixing at least two substances with predetermined relative amounts, filling the substances after mixing into a form, and hardening of the substances to a solid elastic product. According to the invention, the relative amounts of the substances are continuously varied during filling of the form in order to achieve a product with continuously varying hardness within the product. The method is especially useful for production of load absorption and vibration damping.

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Polymer product with continuously graduated hardness

Background of the invention

The present invention relates to a method for production of a polymer product according to the preamble of claim 1. The invention further relates to an apparatus for production of a polymer product and to use of a polymer product.

Research and development is ongoing in the field of polymer products in order to improve production processes and product properties. For some products, it is desirable to vary the hardness of the material throughout the product. For this, different production methods have been employed.

For example, from German patent application DE 2 309 861, it is known to vary the density of a polymer foam in a product gradually by a temperature gradient throughout the product. This may be achieved by cooling the product from the outside during the hardening process.

However, for solid polymers, in contrast to foam polymers, a density variation has hitherto only be achieved in the form of different layers in the product. For example, US 4 974 852 discloses a solid golf ball with a three layer hardness variation.

It would be desirable to vary the hardness of a product made of solid polymer continuously in the product.

It is therefore the purpose of the invention to improve production methods for solid polymer products with varying hardness.

This purpose is achieved by a method as mentioned by way of introduction characterised as described in the characterising part of claim 1.

Usually when a polymer product is produced, a set of several substances is mixed in certain relative quantities in order to achieve a product with a specific hardness. In some cases, a different hardness in a product may be produced with this certain set of substances if the relative quantities are chosen differently. Thus, according to the invention, the hardness of a product may be varied continuously in the product by continuously varying the relative amounts of substances in the mixture.

For example, a mixture of isocyanate, 1.4 butandiol, and a polyether polyol with certain relative amounts may produce a hardness of 60 Shore A. Varying the relative amounts of these substances may vary the hardness in the polymerised product between 60 and 115 Shore A. In order to vary the hardness continuously within the product, the relative amounts of substances in the mixture may be varied during the procedure, where the form for the polymer product is filled with the mixed substances. In principle, the filling of the form can be regarded as a stacking of polymer layers with layer thicknesses that are infinitely thin, where the single layers are not mixed in the form due to the viscosity of the mixture.

In order to ensure proper prevention from mixing, a catalyst substance may be added to the polymer, which results in a fast hardening of the polymer that has left the mixing unit and entered the casting form. This way, the polymer mixture may obtain a relatively high viscosity quickly further preventing mixing during the stacking of the polymer layers.

Also, for prevention from mixing of the polymer layers, the a fibrous material may be added to the polymer mixture.

In order to achieve a higher hardness than possible with a certain system, the isocyanate may gradually be substituted with a different type of isocyanate during the mixing process. This way, a large range of hardness variations between 45 Shore A and 60 Shore D or with even higher hardnesses can be achieved within one product.

In the above described mixture, 1,4-butanediol can be substituted by ethylene glycol to achieve a likewise effect. Alternatively, the polyol may be substituted by a polyamine.

Another mixture for varying hardness within a solid product can be achieved by mixing a polyol with ethylene diamine and varying ratios of an isocyanate together with a further stream containing bisphenol A or F epoxy adduct. Also in this case, a variable hardness product would result. In this case, the ethylene diamine would react with isocyanate first, and then the amine terminated urea product would add onto the epoxy intermediate to give the final polymer.

Description of the drawing

The invention will be explained in more detail with reference to the drawing, where

FIG. 1 shows a diagram for continuously varying ratios in a blend of substances,
FIG. 2 shows an apparatus according to the invention,
FIG. 3 shows the apparatus according to the invention with computer control,
FIG. 4 shows vibration dampers,
FIG. 5 shows bend restrictors.

The substances that are presented in the following are to be understood as examples not limiting the principle of the invention.

Below is shown table 1 with relative weight amounts for specific substances used in a method according to the invention. The substances used for illustration are products commercially available from the British company Hyperlast®.

TABLE 1 **Product/ Hardness Shore A**	**Hyperlast 100 Prepolymer 2875021**	**Hyperlast C100/60 Curative 2851024**	**Diprane C Curative 2872012**
60	100	150	0
65	100	135.3	1.7
70	100	116.1	3.9

75	100	102.6	5.4
80	100	87.9	7.1
85	100	73.2	8.8
90	100	51.4	10.6
95	100	44.9	12.1

The Prepolymer, being a clear or slightly turbid liquid, contains isocyanate and polyols that have partly reacted. The Hyperlast C100/60 Curative, also being a clear or slightly turbid liquid, is a mixture of a polyether polyol and a PTMEG polyol. The Diprane C Curative, which is a colourless clear liquid above the melting point of 20°C contains 1.4 butandiol.

By varying the relative amount of the substances a relatively broad variation of hardness can be achieved as is apparent from table 1.

In order to achieve hardnesses in the region between 20 Shore A and 60 Shore A, the following substitutions have to be made. With the starting point of 60 Shore A and changing the hardness towards 20 Shore A, Hyperlast C100/60 is gradually reduced and substituted by a polyol.

Table 2 contains relative volume amounts for specific substances used in a method according to the invention with the corresponding hardness data for a product with this kind of mixture. As is apparent from table 2, an even broader variation of the hardness in the polymer product can be achieved, namely from Shore A hardness 60 to Shore A hardness 115.

<u>TABLE 2</u> Product/ Hardness Shore A	**Hyperlast Prepolymer 7855092**	**Hyperlast 100 Prepolymer 2875021**	**Hyperlast C100/60 Curative 2851024**	**Diprane C Curative 2872012**
60	0	35.71	60	0
65	0	37.68	57.8	0.72

70	0	40.58	52.77	1.77
75	0	42.86	49.4	2.6
80	0	45.73	45.13	3.65
85	0	49.02	40.26	4.84
90	0	54.2	32.58	6.72
95	0	56.89	28.58	7.7
100	12.81	41.17	30.35	8.16
105	24.78	26.54	31.95	8.59
110	35.93	12.48	33.49	9.01
115	46.41	0	34.92	9.39

As is apparent from table 1, the relative amount of Prepolymer 7855092 and Prepolymer 2875021 determines the hardness of the final product. The change of the hardness from 60 Shore A to 115 Shore A implies a complete substitution of the Prepolymer 2875021 with the Prepolymer 7855092.

In FIG. 1, the relative amounts of these substances are shown graphically on an arbitrary scale. According to the data in this graph, any hardness in the range 60 Shore A to 65 Shore D can be achieved by varying the relative amounts of the substances. The scale for the hardness is from 60 Shore A to 95 Shore A, with a direct conversion to the Shore D range from 40 Shore D to 60 Shore D.

The curves with the shown hardness range can be extended to at least 85 Shore D by extending the curves in a linear fashion, where the curves have slopes as between hardness 60 Shore D to 65 Shore D.

The mentioned mixture has the further advantage that the polymerisation and hardening is roughly temperature independent in the range between 20°C and 140°C, where, however, a process temperature of between 60°C and 100°C is preferred.

An apparatus for production of a product by a method according to the invention is shown in FIG. 2. The apparatus comprises a number of tanks 201 with different sub-

stances to be mixed in the mixing unit 202. Each of the tanks 201 is connected to a feeder unit 203 with a frequency regulated pump unit 204 and a flow control unit 205 to assure that only the desired amount of substance is fed to the mixing unit 202 before the mixture is filled into the polymer casting form 309 as illustrated in FIG 3. Each of the pump units 204, as shown in FIG. 2, is motor driven, where the motor 206 is frequency controlled to variable pumping speed. The flow into the mixing unit 202 is regulated by a number of valve arrangements 206.

The apparatus according to the invention can be controlled by a computer 301, which is illustrated in FIG. 3. A Programmable Logic Controller (PLC) 302 connected to the computer 301 via an interface 303. The PLC 302 has a user interface 304 to indicate the state and functioning of the apparatus and to allow the operator to change parameters for the polymer casting process. Via the PLC 302, the pumping speed of the pump units 204 is controlled by frequency adjustment of the motors 206, as shown in FIG. 2. The actual rotation frequency of the motor 206 is communicated to the computer 301 via an encoder 305, shown in FIG. 2 and in FIG. 3, a frequency converter 306, and the PLC 302. The frequency converter 306 also translates the command for the frequency adjustment as received via a connection 307 from the PLC 302 to the motor 206. The frequencies for the individual motors, may be logically linked 308 by the frequency converters 306, 306', 306'', 306''', which also may be functionally linked to a common communication network (not shown).

The flowing speed of the different substances to be mixed is calculated by the computer 301. For example, this can be achieved by interpolation between the data as shown in Table 2. From these data, a polynomial equation can be calculated which describes the continues variation of the flow speed for the different substances by regulation of the speed for each of the pump motors 206.

Being able to produce elastomer products with continuously varying hardness within the product, several known problems may be solved.

A first problem to be solved is in connection with shock or vibration dampers. Examples are shown in FIG. 4a for a translational damper 401 and in FIG. 4b for a rotational damper 401'. Those dampers 401, 401' are often constructed as a polymer block 401, 401' between two metal parts 402, 403 or 402', 403', respectively, to which the polymer block 401, 401 is vulcanised. A typical problem is damage of the dampers 401, 401' after relatively short term use due to cracks in the transition 404 between the polymer 401, 401' and the metal parts 402, 403. Soon after a crack has occurred, the polymer 401, 401' breaks along this crack which evolves through the polymer block 401, 401'. The lifetime of such a vibration damper can be prolonged with a hard polymer. However, a hard polymer does not damp sufficiently, so the chosen hardness is a compromise between the requirements for the damping properties and the requirements for reliability and lifetime of the damper.

This problem is solved by an elastomer block 401, 401' produced with a continuous hardness variation according to the invention. The polymer in the transition 404 near the metal part 402, 403 is chosen with a high hardness in order to omit evolving cracks in this part, while the middle part 405 of the elastomer block 401, 401' is of a much softer polymer in order to have optimum damping properties.

It has to be emphasised at this point, that the problem with the vibration dampers is not solved satisfactory, if a hardness variation in the polymer block 401, 401' is chosen in layers with constant hardness, for example a three layer arrangement with a soft layer in the middle 405 of the polymer block 401, 401' and two hard layers attached to the metal 402, 403, because cracks may occur in the interface between the layers with different hardness already after short term use. The continuous variation is essential for optimum functioning and reliability.

A second problem to be solved is in connection with pipe joints, as illustrated in FIG. 5a, where a pipe 501 with a flange 502 is fastened to an underlying coupling unit 503. Transversal forces on the pipe 501 may lead breakage of the pipe 501 from the flange 502 or the underlying coupling unit 503. In order to support the pipe around the joint, a stiffening polymer pipe sleeve 504 as a bend restrictor may be employed for stress

and load absorption. Due to a certain stress exerted on the sleeve, cracks may occur in the interface region 505 between the sleeve 504 and the flange 502, which finally leads to breakage of the sleeve 504. Also this problem may be solved with a sleeve 504 that has a high hardness in the interface region 505 and a lower hardness in the outer region 506.

Especially in off shore industry, where long pipes 501 are used for oil or gas transportation from the bore hole 508 to the platform, as illustrated in FIG. 5b, a problem exists, where pipes 501 break due to transversal and longitudinal load. In order to prevent the pipe 501 to break at the interface at the bottom 509 of the sea, the pipe 501 may coupled to a coupling unit 503 which is surrounded by an elastic sleeve 504 as a bend stiffener and bend restrictor in order to damp motions and to absorb stress and load exerted on the pipe. This elastic sleeve 504, according to prior art, may be subject to cracks in the interface 505 between the sleeve 504 and the coupling unit 503 or the sleeve 504 and the pipe 501 in the same manner as described above. Therefore, also in this case, a substantial improvement is achieved, if the sleeve 504 for such pipelines 501, where the sleeve 504 may weight several tons, has a continuous hardness variation. Due to the much better reliability and long term stability, a pipeline sleeve 504 according to the invention may be constructed much smaller than existing sleeves for this purpose, which results in a substantial reduction in labour and cost for this kind of elastomeric solutions.

A further application for the invention is production of vacuum hoses. Such a hose must have two primary characteristics. It must be stiff enough to withstand the pressure from the outside against the low inner pressure and it must still be able to bend. Such a hose can be produced according to the invention by continuously varying the hardness of the polymer in the direction along the hose, such that the hardness variation is a alternating function along the direction of the hose. The hose will thus consist of hard rings which are connected by softer and flexible rings, where the hardness varies gradually between the hard and the soft rings.

Apart from the examples, where the invention leads to a substantial improvement, a method for production and a product according to the invention is useful for toys, sports training equipment, vehicle equipment, helicopter equipment, aeroplane equipment, and other marine or oil field equipment.

CLAIMS

1. Method for production of a polymer product with varying hardness comprising adding together and mixing a number of substances with predetermined relative amounts, said number being at least two, filling said substances after mixing into a form, and hardening of said substances to a solid elastic product, characterised in that the relative amounts of at least two of said number of substances are continuously varied during filling of said form.

2. Method according to claim 1, characterised in that said varying hardness is at least one from the group consisting of
between 20 Shore A and 115 Shore A
between 40 Shore D and 85 Shore D,
between 20 Shore A and 85 Shore D.

3. Method according to claim 1 or 2, characterised in that said number of substances are taken from the group consisting of bisphenol, butandiol, ethylene diamine, ethylene glycol, epoxy, epoxy adduct, isocyanate, polyol, polyamine,

4. Method according to claim 3, characterised in that at least three substances are mixed,
- the first substance being a polyol or a polyamine,
- the second substance being 1.4 butandiol, ethylene glycol, or ethylene diamine, and
- the third substance being a first isocyanate.

5. Method according to claim 4, characterised in that the relative amount of said first isocyanate is constant.

6. Method according to claim 4 or 5, characterised in that said adding of said first isocyanate results in a hardness of between 60 Shore A and 95 Shore A.

7. Method according to claim 4, characterised in that during said adding process said adding of said first isocyanate is gradually substituted with the adding of a second isocyanate, wherein the change from said first isocyanate to said second isocyanate is performed in a continuous way.

8. Method according to claim 7, characterised in that gradually substitution results in a hardness variation between 60 Shore A and 115 Shore A.

9. Method according to claim 7, characterised in that said adding of said second isocyanate results in a hardness of between 40 Shore D and 65 Shore D.

10. Method according to any one of the claims 1 - 4, characterised in that said number of substances further comprises bisphenol A or F epoxy adduct.

11. Method according to any one of the claims 1 - 9, characterised in that a catalyst is added for fast polymerisation.

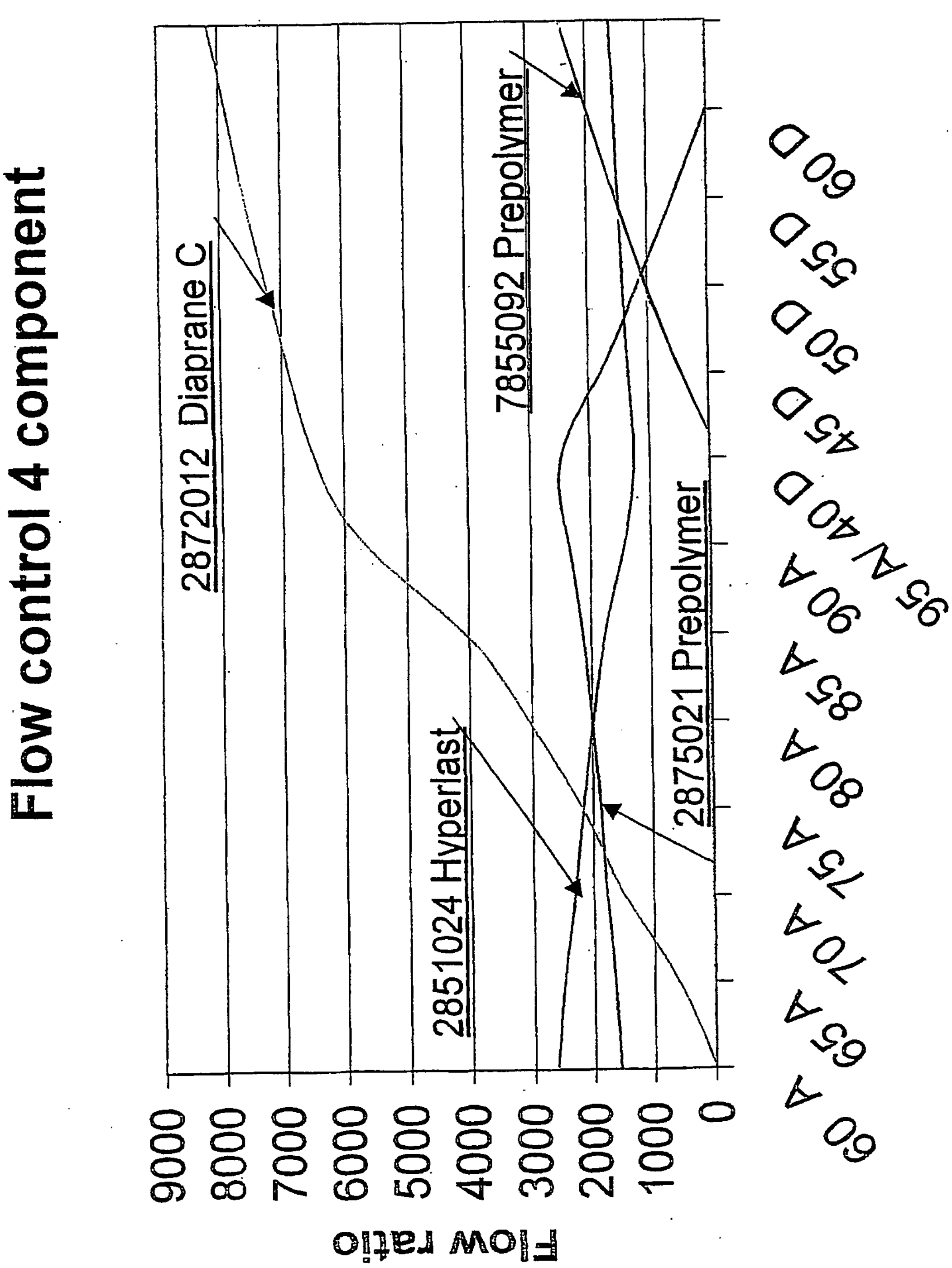
12.Method according to any of the claims 1 - 10, characterised in that the method further comprises adding fibrous material before or during filling of the substances into the form.

13. Apparatus for production of a solid product with continuously varying hardness comprising at least two substance feeding units for substance feeding into a mixing unit, a feeding control for controlling the substance feeding speed, said speed being continuously variable, and a filling unit for filling said polymer mixture from said mixing unit into a product form for hardening of said substances.

14. Apparatus feeding speed for each feeding unit is computer controlled and varied by frequency adjustment the driving unit for the feeding unit.

15. Solid polymer product with continuously varying hardness within the product.

16. Use of a method according to any of the claims 1 - 12 for production of at least one from the group consisting of toys, sports training equipment, vehicle equipment, helicopter equipment, aeroplane equipment, marine equipment, oil field equipment, couplings for rotary shafts, shock dampers, vibration dampers, hoses, especially vacuum hoses, pipe couplings, and pipe sleeves for stress and load absorption, especially bend stiffeners and bend restrictors.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7000
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4000
3000
2000
1000
0
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65 A
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75 A
80 A
85 A
90 A
95 A/40 D
45 D
50 D
55 D
60 D
2872012 Diaprane C
7855092 Prepolymer
2851024 Hyperlast
2875021 Prepolymer

FIG. 1

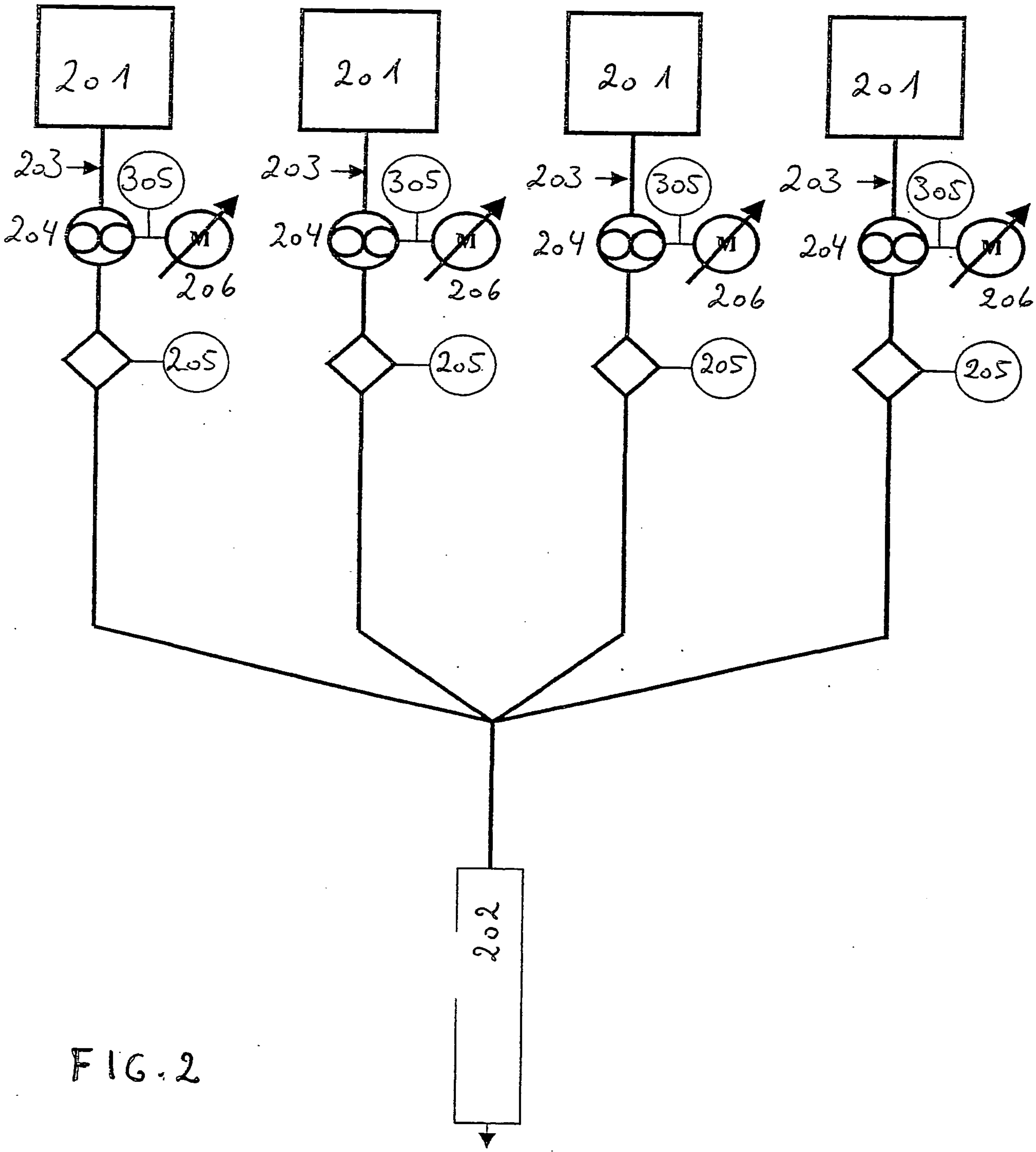
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FIG. 2

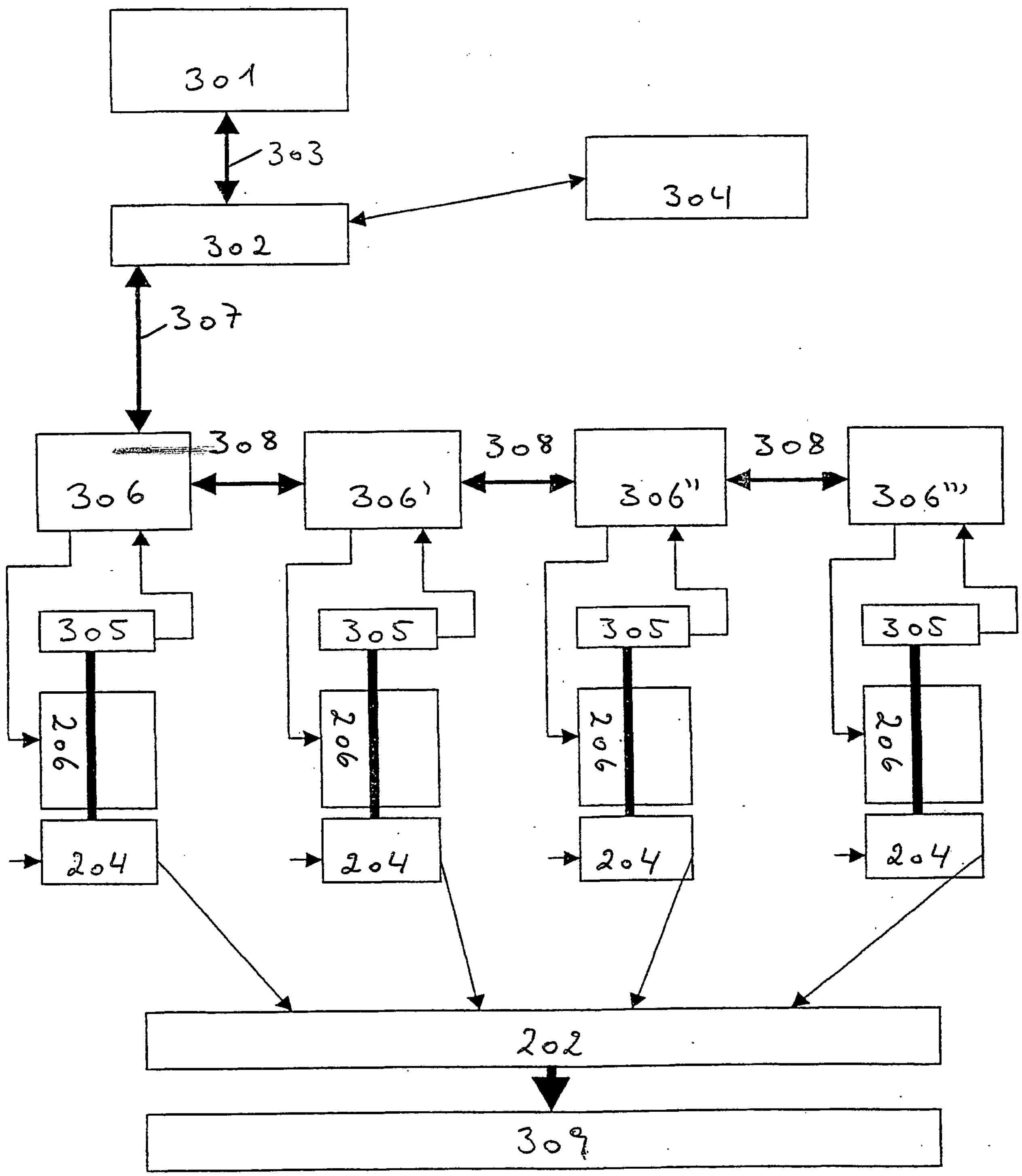
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FIG.3

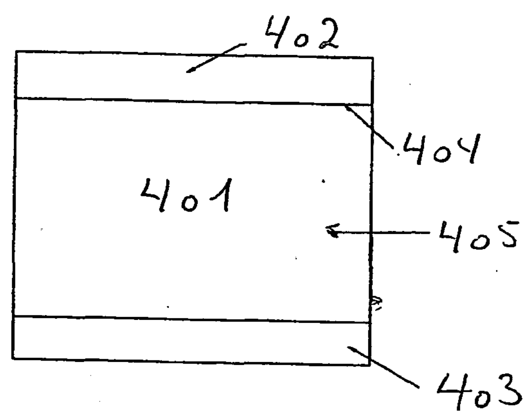

FIG. 4a

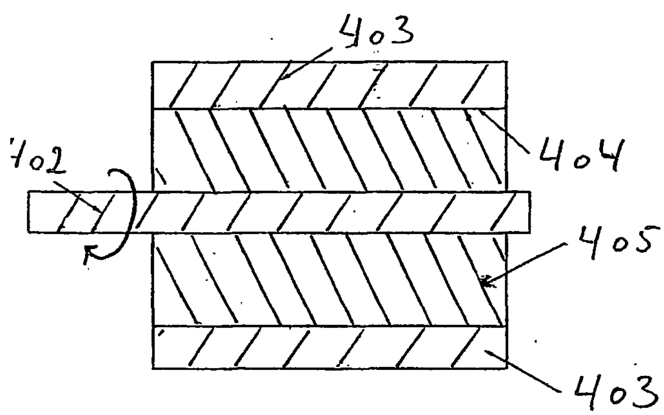

FIG. 4b

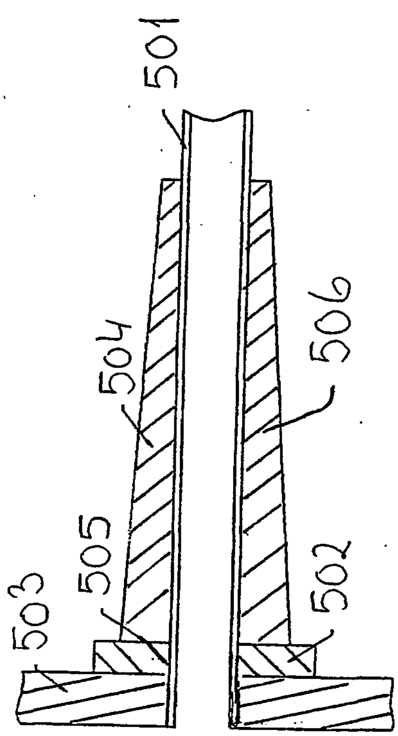

FIG. 5a

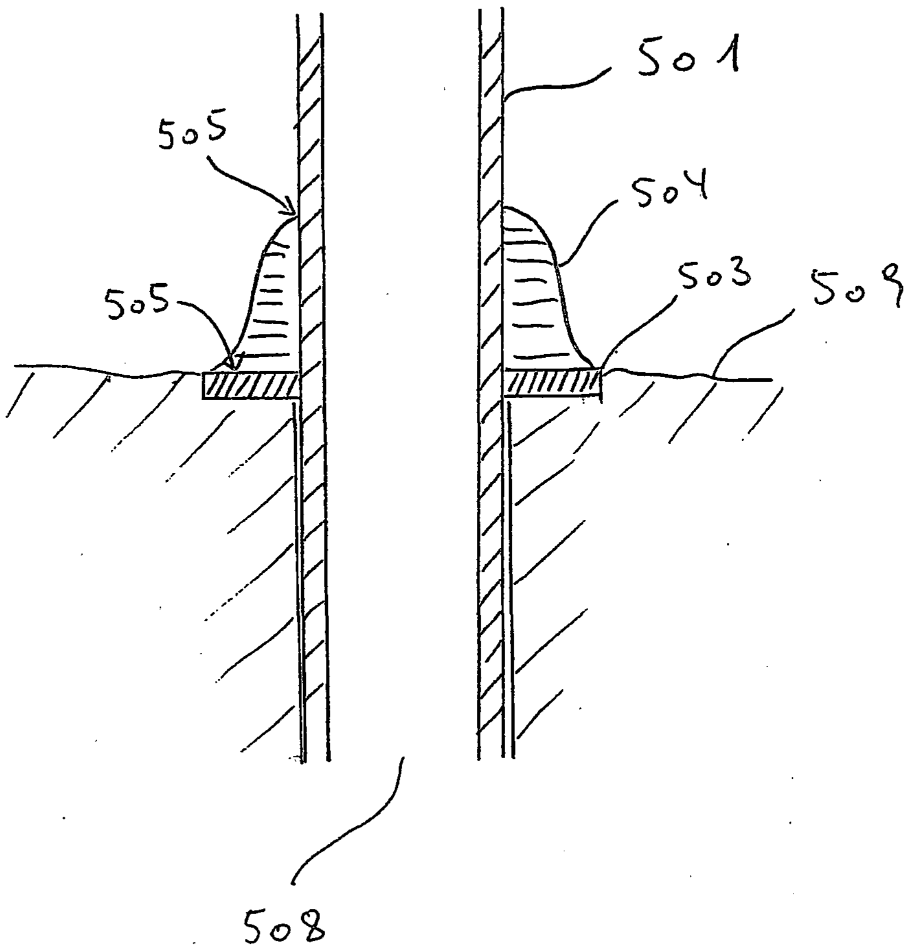

FIG. 5b

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 01/00670

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B29C 31/10, B29C 39/24, B29C 67/24, B29C 45/18, C08J 5/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B29C, C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI-DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SE 321343 B (DUNLOP RUBBER CO LTD), 2 March 1970 (02.03.70), page 1, line 10 - line 15; page 2, line 7 - line 13, figures, claims --	1-10,13-15
X	GB 2102331 A (PERMABOND ADHESIVIS LTD), 2 February 1983 (02.02.83), page 1, line 17 - line 23, figure 1, claims, abstract --	1-3,10-15
X	EP 0771642 A1 (METTON AMERICA INC), 7 May 1997 (07.05.97), page 4, line 2 - line 11; page 5, line 19 - line 21; page 5, line 42, page 8, line 35 - line 39; figures, claims, abstract --	1-3,13-15

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
4 April 2002	09-04-2002
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Monika Bohlin/EK Telephone No. +46 8 782 25 00

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT
Information on patent family members

28/01/02

International application No.
PCT/DK 01/00670

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